

Environmental Effects in the
Atmospheric Corrosion of Zinc

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ENVIRONMENTAL EFFECTS IN THE ATMOSPHERIC
CORROSION OF ZINC

by

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ABSTRACT: The Bureau of Mines, U.S. Department of the Interior, as part of the National Acid Precipitation Assessment Program, is conducting a field exposure program to measure the corrosion damage on commonly used structural metals and the incremental effects of acidic deposition and other environmental variables. Corrosion damage, air quality, rain chemistry and meteorology are being continuously measured at 5 site in the Eastern and Midwest U.S. for periods up to 84 months. Corrosion damage on zinc for periods up to 36 months was determined from weight-loss measurements, analysis of corrosion film chemistry and precipitation runoff chemistry. The long-term zinc corrosion film may consist of a stable inner layer sensitive to atmospheric SO_2 , and a nonprotective outer layer. Synergism between SO_2 and NO_2 may occur. Dry deposition of SO_2 and NO_2 is significant. Zinc losses from the corrosion film are proportional to H_L . Covariance between many air quality and rain chemistry variables may be sufficiently low as to avoid, to a considerable degree, problems in developing linear regression models of corrosion damage.

KEY WORDS: corrosion, atmospheric corrosion, zinc, air quality, rain chemistry, meteorology, corrosion film chemistry, runoff chemistry, hydrogen ion load, sulfur dioxide, nitrogen oxides, acidic deposition, wet deposition, dry deposition

As part of the research activities of Task Group VII-Effects on Materials, within the National Acid Precipitation Assessment Program (NAPAP), the Bureau of Mines (BOM), U.S. Department of the Interior, is conducting a field exposure program to measure corrosion damage to commonly used structural metals. The purpose of this research is to determine the effects of acidic deposition and other important environmental variables on corrosion damage, and to establish a data base for testing various physicochemical models of corrosion damage and from which dose/response relationships or damage functions can be developed. Accurate assessment of environmental effects on corrosion damage requires concurrent measurements of air quality, rain chemistry, and local meteorology. Five sites where these measurements are continuously recorded have been established in the East, Northeast, and Midwest of the United States. Two of these sites have been operated since 1982. Metals being studied by the BOM at these sites are 1010 carbon steel, Cor-Ten A, 110 copper, 191 zinc, 3003-H14 aluminum, and two coated-steel products, galvanized steel and Galvalume. Other weathering studies are being conducted at these sites by the Environmental Protection Agency on industrial and household paints, and the National Park Service and Geological Survey on dimension stone. A description of the field exposure program, including onsite monitoring activities and aerometric and rain chemistry characteristics, has been reported (1).

Zinc corrosion data from this program are the focus of the present paper. The atmospheric corrosion of zinc has been widely studied in

laboratory and field exposures (2-7). Much of a general nature is known about the zinc corrosion process. However, specific details of the chemical and physical processes, and complex interactions between these processes, which allow one to assess changing environmental conditions and determine their effect on corrosion are not nearly as well known. In this paper, seasonal variations in air quality and rain chemistry at four of the exposure sites are described. Covariance between these environmental variables that may affect linear regression models of atmospheric corrosion are examined. The effects of environmental factors on the dissolution of the corrosion film and their implications concerning corrosion film chemistry are discussed. Finally, evidence is presented from 3-year exposures that suggest, as a possible explanation, the corrosion film consists of an outer layer that is relatively unprotective and an inner layer sensitive to SO_2 , and perhaps other environmental species, that controls the corrosion process in long-term exposures.

EXPERIMENTAL PROGRAM

Field exposure corrosion tests are conducted at five sites which are located at Research Triangle Park, NC, Washington, DC, Chester, NJ, Newcomb, NY, and Steubenville, OH. Air quality, rain chemistry, meteorology, and particulate chemistry are monitored continuously at these sites. A combination of federal, state, local, and private organizations are conducting the environmental monitoring activities (1). A smaller

methods site for trials of new experiments is operated without environmental monitoring at the BOM Avondale Research Center. The test site on the roof of the West End Library in Washington, DC, figure 1, is typical of the sites at all of the locations. Three types of exposure experiments -- boldly-exposed, sheltered, and runoff -- are being conducted on panels of rolled zinc (191 zinc) at these sites (1). Only the boldly-exposed and runoff experiments are discussed here.

Boldly-exposed measurements

Zinc samples are prepared and exposed using ASTM recommended procedures for atmospheric corrosion tests(1). Exposed samples are mounted in a rack so that they face south at a 30° incline with the horizon. Weight-loss panels measure 10x15-cm (4x6-inches) and are exposed in triplicate. Microanalysis coupons, intended for subsequent surface analyses, are exposed with the weight-loss panels and measure 2.5x4.5-cm (1x1.75-inch). Samples are exposed for periods of 1, 3, 12 and 36 months; exposures up to 84 months are in progress. In addition, pairs of samples with one side masked off are being exposed to measure skyward and groundward effects. Corrosion film weights are measured as well as corrosion weight loss. Corrosion film compositions are measured by wet chemical analysis of the weight-loss panel stripping solutions (1). Zinc loss in precipitation runoff from the panels is computed by the difference between the zinc weight loss and the amount of zinc retained in the corrosion film.

Runoff measurements

This experiment is conducted only at the Washington, DC site. It measures directly wet and dry deposition on the zinc panel surface. The runoff experiment is similar to the boldly-exposed experiment except that it involves only one large zinc panel and that panel is fitted with a special polyethylene tray to collect all of the precipitation draining from the panel. This runoff is then funnelled into a container for subsequent chemical analysis (8). The zinc runoff panel measures 0.2 m^2 (1x2-foot). A type 304 stainless steel panel is used as a control to determine runoff effects from a relatively inert surface for comparison with the zinc runoff results. Runoff samples from the zinc and stainless steel panels are collected monthly for analysis, as is the rain chemistry sample from the site. The monthly runoff samples and the rain chemistry samples are analyzed at Research Triangle Institute for H, Na, K, Ca, Mg, NH_4 , Cl, NO_3 , SO_4 , and Zn. A skyward side corrosion experiment is conducted concurrently with the runoff experiment to provide data on the weight loss and corrosion film composition of the zinc runoff panel. With these data, a mass balance on the runoff panel corrosion film yields directly the amount of dry deposition on the panel,

$$D_i = R_i + A_i - W_i. \quad (1)$$

where, for the i-th chemical species and measured per unit of runoff panel surface area,

W = wet deposition; the input to the panel surface primarily from rain and snow; determined from the analysis of the rain chemistry sample,

A = corrosion film accumulation term; determined from the composition of corrosion film on the skyward side corrosion panel exposed for the same time as the runoff panel,

R = runoff; the output from the panel surface; contains constituents from both wet and dry deposition and plus those washed from the corrosion film; determined from the analysis of the runoff sample,

D = dry deposition term; the input to the panel surface from dusts, aerosols, and adsorption of gaseous species.

Corrosion product characterization

The corrosion films on selected zinc microanalysis samples have been examined by scanning electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, ion scattering spectroscopy and thermogravimetric analysis (TGA) and the results reported elsewhere (9).

Additional TGA analyses were performed on zinc samples exposed 1 to 36 months. One set of measurements was made in He at atmospheric pressure. A second set was done under vacuum using a Veeco SPI-10 monopole residual gas analyzer (RGA) to identify and measure the gases produced by thermal decomposition of the corrosion film. All measurements were conducted using a Cahn RH electrobalance with a Cahn Mark II time derivative computer. Both weight-loss and weight-loss rate were recorded at a nominal heating rate of $5^{\circ}/\text{min}$ over the temperature range 40° to 250°C . Measurements of gas composition by the RGA and gas pressure with an ionization gage were made at 5 min intervals during the TGA run.

RESULTS AND DISCUSSION

Environmental Variables

Most of the air quality and rain chemistry parameters measured exhibited typical annual, if somewhat noisy, cycles at each of the sites. These observations were made by inspection, using roughly 3 years of monitoring data, and are meant only to convey a sense of the periodic nature of the data.

A. Air quality - Average gaseous pollutant concentrations computed for the 24 month period June 1983 - May 1985 are given in Table 1. Except for SO_2 at the Washington, DC, site, these values are similar to those reported earlier (1). The Washington, DC, SO_2 value represents a 35 pct reduction from 1982 levels. High nitrogen oxide levels are characteristic of the DC site and should be considered in terms of possible synergistic corrosion effects involving SO_2 and NO_2 at low relative humidities (10-11). Figure 2 is a plot of monthly average SO_2 concentrations for the Washington, DC, and New York sites. The cycle of maximum pollution levels in the winter and minimum levels in the summer is in good agreement with historic patterns related to regional energy demands. A similar pattern exists for NO and NO_2 at each of the sites with two exceptions. Nitrogen oxides are too low at the New York site for any pattern to be observed. Nitrogen dioxide is high all year at the Washington, DC, site and

exhibits no periodic behavior. Ozone has a cycle which is shifted by 6 months from those for SO_2 , NO , and NO_2 , and exhibits maximum concentrations in the summer and minimum concentrations in the winter.

B. Rain chemistry - Monthly ion loading, defined as the product of ion concentration and monthly rain volume divided by the cross-sectional area of the rain collector, is used here in preference to ion concentration because ion loading gives a measure of the total exposure to an ion species. Figure 3 is a plot of monthly hydrogen ion loads at the Washington, DC, and New York sites. Hydrogen ion load peaks during the summer and is a minimum in the winter. This cycle is roughly 6 months out of phase with the cycle for SO_2 shown in Figure 2. Other ionic species important in the wet deposition of acidic species, such as SO_4 , NO_3 , and NH_4 , follow the same cycle as the hydrogen ion.

Table 2 lists correlation coefficients computed from monthly air quality and rain chemistry data obtained at each site over a two year period, July 1983 - June 1985. The correlation between rain volume (V) and the hydrogen ion load (H_L) is perhaps of the most interest. One would expect, since H_L includes rain volume in its computation, that the correlation would be strong. Instead the correlation coefficient ranges from .42 for the Washington, DC, site for .84 at the New Jersey site, i.e., from a weak correlation to a moderately strong correlation. Similar values are observed for the interactions $V\text{-SO}_{4L}$ and $V\text{-NO}_{3L}$. Table 2 also shows high

correlations between ions associated with acidic deposition, H_L-SO_{4L} and $H-NO_{3L}$, and with atmospheric aerosols, $NH_{4L}-SO_{4L}$ and $NH_{4L}-NO_{3L}$. On the other hand, there is no correlation or only a relatively weak negative correlation for SO_2-SO_{4L} , NO_X-NO_{3L} , H_L-SO_2 , and H_L-NO_X . These results suggest that problems arising from covariance (or multicollinearity) in developing linear regression models of corrosion damage may be avoided to a considerable degree for a number of air quality and rain chemistry variables, including rain volume and the hydrogen ion load.

C. Meteorology - Time-of-wetness (TOW) is often estimated by the time when the relative humidity (RH) exceeds 80 pct and the temperature is above freezing (12). Annual TOW values computed in this was from 1983 RH data gave the following results (in hours): North Carolina - 2800; Washington, DC - 2160; New Jersey - 3390; and New York - 5980.

Zinc corrosion damage has been shown to vary directly with the atmospheric concentration of SO_2 (2, 4, 6, 10, 13-15). In one study, Schikorr (15) shows that the monthly average corrosion rate of zinc closely followed the annual cyclic variation in SO_2 concentration. The corrosion data from the present study were examined for seasonal trends. None were found in the data from the North Carolina, Washington, DC, and New Jersey sites for exposures of 1, 3, or 12 months. This probably reflects the importance of TOW and other environmental factors in the corrosion process. (Temperature and humidity data is being assembled for each site but is not yet available.) On the other hand, data from the New York site exhibited cyclic behavior for all three exposure periods. Maximum corrosion rates for monthly exposures were observed in September and minimum corrosion rates in January-February. This does not coincide with the patterns established for any of the air quality or rain chemistry variables. However, it also probably reflects the importance of TOW in that freezing winter temperatures at the New York site prevent significant corrosion from occurring.

Corrosion Film Chemistry

In the absence of acidic deposition and marine influences, the corrosion of zinc in the atmosphere is considered to involve first the formation of zinc oxide or hydroxide (9). Equilibration with atmospheric CO_2 then leads to the formation of basic zinc carbonates (16). Various reactions

and equilibria involved in these processes are shown schematically in Fig.

4. Loss of zinc from the corrosion film would appear to occur by two routes. In clean environments, those free of acidic deposition, the Zn(OH)_2 or basic zinc carbonate can dissolve in precipitation and wash from the surface. When acidic species are present in wet or dry deposition, a second route is available.. This involves reaction of hydrogen ion with the basic zinc corrosion product to form a soluble salt, such as ZnSO_4 , that can be washed from the surface. In this neutralization reaction, 2 moles of H^+ are needed to free a mole of Zn from Zn(OH)_2 whereas presumably only one mole of H^+ is required for ZnCO_3 because the soluble bicarbonate ion is formed (9). The rate of the neutralization reaction will depend on the kind of acidic species delivered to the zinc surface, its rate of delivery in wet or dry deposition, its residence time on the surface, and the presence of other species that may influence the reaction.

Zinc corrosion film weights, which are roughly related to corrosion film thickness, are shown in Fig. 5. Each vertical bar represents data from 25 tests in the one month exposures, 14 in the 3 month exposures and 11 in the 12 month exposures. The corresponding number of available tests for the Ohio site are 12, 4 and 1. The horizontal lines dividing the bars represent the mean film weights computed from these tests. The horizontal lines for the 3 year exposure represent the one test completed at each of the sites except for Ohio. The considerable dispersion in the film weights probably reflects the sensitivity of the corrosion films to

conditions in the environment. All of the samples removed from the field had measureable corrosion films. The minimum measured corrosion film weights at each site increased with exposure time. The average corrosion film weights increased with time. The increase with time was rapid for the Washington, DC, site, particularly after 3 months exposure, moderate for the New Jersey and New York sites, and slow for the North Carolina site. The substantial corrosion film weight present after only 1 month exposure would suggest that the corrosion product forms rapidly and that the zinc surface is covered within hours or days.

Zinc corrosion rates are shown in Fig. 6 for the same set and number of tests presented in Fig. 5. The vertical bars represent the range of the mean corrosion rates observed in the given exposure period. The solid black bars represent the standard deviation computed from the three replicate measurements in each test and indicates the precision of the measurements. The midpoint of the solid bar locates the average corrosion rate computed from the means for all the tests at a given site in a given exposure period. The wide dispersion in the corrosion rates for the shorter exposures indicates the importance of the environmental conditions at the initial exposure. Such variations in corrosion rate are common in much of the field data reported for short exposures (1-5). Most of these

variations have damped out after 1 year. Except for the Washington, DC, site mean monthly corrosion rates fall by a factor of 2 after 3 months exposure and by a factor of 2 again after 12 months exposure, indicating that the initial corrosion product forms a protective layer on the zinc. However, from 1 year to 3 years there is little decrease in the corrosion rate at the New York, New Jersey, and North Carolina sites and the corrosion rate actually increases by 50 pct at the Washington, DC, site. This, coupled with the increase in film weight shown in Fig. 5 would suggest that the film growth in longer exposures does not contribute to a more protective corrosion film.

All of the zinc corrosion films analyzed by TGA, ranging from films formed in 1-month to 3 year exposures, gave similar weight-loss and derivative curves. These involved a gradual but increasing weight-loss with increasing temperature and then, for measurements in He at atmospheric pressure, a rapid weight-loss from 200° to 250° C. For measurements in a vacuum, as in Fig. 7, the rapid weight-loss began at temperatures about 20° C cooler. (Temperature control was more difficult in the vacuum used for the TGA-RGA measurements. This lead to fluctuations in the heating rate which prevents direct comparison of the weight-loss and derivative curves in Fig. 7.) The observed weight-loss behavior was consistent with a film composed of a basic zinc carbonate $\text{ZnCO}_3 \cdot n\text{Zn(OH)}_2$. It indicates that conversion of the initial Zn(OH)_2 into the basic zinc carboate begins as soon as the initial corrosion product forms. Measurements on samples exposed 1 month and 3 years at the

Avondale (MD) site using the combined TGA-RGA technique showed that CO_2 and H_2O were produced by the thermal decomposition, Fig. 7, direct evidence that the corrosion product consists of both Zn(OH)_2 and ZnCO_3 . It is reasonable to assume that the partial pressures for CO_2 and H_2O shown in Fig. 7 are proportional to the molar production of these gases from the corrosion film as a function of temperature (and roughly of time). The integrated area under the curves, after establishing a reasonable baseline, should then be proportional to the total molar production of these gases. The ratio of areas from Fig. 7 is $\text{H}_2\text{O}/\text{CO}_2 = 1.5$. This corresponds to a basic zinc carbonate film composed of $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2$ (16).

The wet and dry deposition of S, N (as NO_3), Ca, and Na on zinc exposed 1 and 3 months at the Washington, DC, site is summarized in Table 3. Values for the stainless steel surface are included for comparison. These values were computed from the runoff measurements using Eq. 1. Ca, which is a constituent of dusts and ash, not surprisingly is primarily delivered to the panels as dry deposition. Na, which is often explained as constituent of sea salt but is also a significant constituent in ash (17), is delivered in roughly equal amounts in wet and dry deposition. The dry deposition of Ca and Na on the zinc and stainless steel surfaces is similar and suggests that, at least in short exposures, both surfaces have roughly the same efficiency as collectors of particulates. Furthermore, if it is assumed that the adsorption of NO_x and SO_2 on the stainless steel is small by comparison to the dry deposition of nitrate and sulfate aerosols, one can interpret the increased dry deposition of S and N on the zinc as

a result of SO_2 and NO_x absorption by the zinc corrosion product. In the case of sulfur, these figures clearly indicate that the corrosion film is a strong absorber of SO_2 . This fact is further accentuated by knowing that the measurements were made in the June-August period when SO_2 values are lowest at the Washington, DC, site and wet deposition of sulfate is highest. Despite these conditions, the S deposited by dry deposition was nearly as great as that by wet deposition. A similar analysis for N shows that NO and NO_2 , which generally have much higher atmospheric concentrations than SO_2 at this site, are less readily absorbed by the corrosion film. Interestingly, the measured accumulation of S in the corrosion film after 1 month exposure was, on average, 8 mol pct compared to the amount of zinc in the film. It remained at this level in longer exposures and, after 3 years, the S concentration had increased to only 10.0 mol pct.

The results of the runoff measurements in terms of solution chemistry are shown in Fig. 8. The lines in this figure are simply a graphical representation of the different equilibria shown in Fig. 4. The small cross-hatched area represents the range of pH and Zn concentrations observed in the runoff samples collected over a seven month period, June-December 1985, at the Washington, DC, site. The bracket at the lower left corner of the figure shows the pH of the incident rain. The brackets above it show the range of Zn^{2+} concentrations that would result if all the H^+ neutralized either $\text{Zn}(\text{OH})_2$ or ZnCO_3 . In addition to a curve describing the solubility (dissociation) of ZnCO_3 , there is one for amorphous and $\alpha\text{-Zn}(\text{OH})_2$.

Pourbaix (18) indicates that these forms of Zn(OH)_2 are more likely to exist under the neutral to slightly acid conditions that occur on the outer surface of the corrosion film than the less soluble $\epsilon\text{-Zn(OH)}_2$. In any case, the solubility of the corrosion product would appear to be orders of magnitude higher than the concentrations which exist in the runoff. Saturation of the runoff in Zn ions, even in a thin boundary layer adjacent to the film surface, would appear unlikely. The narrow range of near neutral pH values observed for the runoff, 6.58 to 6.74, simply indicates that the corrosion film has reacted with practically all of the acidic species present in the runoff.

Runoff data are reported in Table 4 for the June-December 1985 measurements where H_L is the monthly hydrogen ion load, V_L is the monthly rain load, and R is the Zn lost from the corrosion film in runoff. These data were fit by least squares to the 2-parameter model

$$R = (\alpha_1 + \alpha_2 [H^+])V_L, \quad (2)$$

where $H_L = [H^+]V_L$, and $[H^+]$ is the hydrogen ion concentration in the incident rain. This equation was reported in a slightly different form earlier (9). α_1 represents the solubility of the corrosion product in neutral precipitation, and α_2 represents the number of grams of Zn dissolved from the corrosion film per gram-equivalent weight of hydrogen ion consumed by reaction with the zinc corrosion product. In fact, these two processes,

dissolution and neutralization, occur concurrently and separating them as variables, as in equation 2, is a simplification of that relationship. Treatment of H_L and V_L as independent variables to compute α_1 and α_2 should be straightforward since the correlation between them is weak for the Washington, DC, site, Table 2. The results of these calculations are shown in Table 5 using H_L and V_L alone as explanatory variables and then together. The t-scores indicate the α 's are significant for each of these cases, but the higher R^2 for the combination of H_L and V_L would indicate this is the preferred model. Based on the latter results, about 3.2 mg Zn is dissolved from the corrosion film per L of precipitation. The value of α_2 , 34.2, is quite close to the theoretical value of 32.7 for the dissolution of $Zn(OH)_2$ and suggests that $Zn(OH)_2$ is the constituent being neutralized in the corrosion film at the Washington, DC, site in short exposures. Equation 2 was also fitted to the 3, 12, and 36 month runoff data from the boldly-exposed weight-loss measurements at the North Carolina, Washington, DC, New Jersey, and New York sites. The results are shown in table 5 in the same format used for the runoff data. While H_L and V_L alone are both significant explanatory variables, only the H_L term is significant when they are combined. For this reason and the slightly higher R^2 , H_L was chosen as the explanatory variable for the long-term data. These data and the fitted curve are plotted in Fig. 9. The slope of 93.2 is higher than the theoretical slope of 65.4 for the dissolution of $ZnCO_3$ and reflects perhaps contributions from acidic species that are

covariant with H_L . The higher slope also indicates that, per mole of hydrogen ion, the zinc corrosion film is being dissolved more rapidly in the long-term exposures at the 4 sites than in the short-term exposure of the Washington, DC site.

Weight-Loss Measurements

The loss of corrosion products in the runoff as a result of hydrogen ion and other acidic species, particularly the higher loss rate in longer exposures, raises the question of whether the corrosion film is stripped totally from the panels in long exposures. The results in Figs. 5 and 10 suggest this is not happening. Zinc weight loss is shown in Fig. 10 as a function of zinc runoff in 1 and 3 year exposures at 4 sites plus a 3 year exposure at the Avondale (MD) methods site. A mass balance on the corrosion film shows that the zinc weight-loss from the panel, M , is given by

$$M = M_A + M_R \quad (3)$$

where

M = Zn weight-loss, mg/dm^2

M_A = Zn accumulated in the corrosion film; determined from corrosion film analyses, mg/dm^2 .

M_R = Zn runoff; measured as the difference $(M - M_A)$; mg/dm^2 .

The derivative of equation 3 with respect to M_R is

$$\frac{\partial M}{\partial M_R} = \frac{\partial M_A}{\partial M_R} + 1 \quad (4)$$

and rearranging

$$\frac{\partial M_A}{\partial M_R} = \frac{\partial M}{\partial M_R} - 1 \quad (5)$$

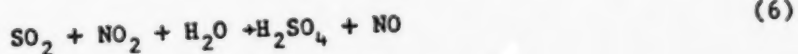
At steady state conditions, when there is no further growth in the corrosion film, $\partial M_A / \partial M_R$ should be 0 and the weight loss of zinc should equal that lost from the corrosion film in runoff, i.e., $\partial M / \partial M_R = 1$. However, the slope in Fig. 10, $\partial M / \partial M_R = 1.35$, indicates that even after 1 and 3 years exposure the corrosion film is continuing to grow, i.e., $\partial M_A / \partial M_R > 0$, and more zinc is being accumulated in the corrosion film. Examining the data in Fig. 10 by site does reveal some differences. The Washington, DC, and New York sites have slopes of 1.65, while that for New Jersey is 1.20 and North Carolina is 1.16. Data for shorter exposures exhibit a lot of scatter but the slopes are higher, indicating the expected trend toward $\partial M / \partial M_R = 1$ with increasing exposure.

Consider Fig. 11, where weight-loss data are plotted versus exposure time for 3 year exposures at each of the sites, and a series of 1 year exposures at the Washington, DC, and North Carolina sites. The short-term data shows a lot of variability which, as noted earlier, is typical of such data for zinc and related to the importance of the environmental condition at the initial exposure. Figs. 5 and 10 show the corrosion film thickness increasing with exposure, particularly in the longer exposures.

Fig. 11 shows the instantaneous corrosion rates leveling off, or in the case of the Washington, DC, site, actually increasing. This is not the result expected of protective corrosion films or exhibited by the corrosion films in short exposures where, an increase in average film thickness produced a decrease in corrosion rate. It would appear that beyond a certain average thickness, the increase in film thickness, particularly the increase in longer exposures, offers no real improvement in corrosion protection. This would suggest, as a possible explanation, that the corrosion film consists of two layers in long exposures, a stable inner layer with considerable control over the corrosion process and a non-protective outer layer which continues to grow. This outer layer would be affected to a greater extent by all of the weathering processes which affect the corrosion film — TOW, H_L , dry deposition, runoff, basic carbonate formation. In short exposures, while the two-layer structure is developing, these processes alter the corrosion film in ways that affect the corrosion process. Hence, the strong influence of environmental factors on corrosion performance observed in exposures up to a year. In longer exposures, the two-layer structure is well developed and many of the environmental influences damp out.

The existence of a two-layer structure in longer exposures is certainly suggested by the ordering of the 3 year weight-loss values, Fig. 11, an ordering which is totally different from that which would be inferred from the shorter-term data. For the first time the ordering of metal damage

would appear to be related to atmospheric SO_2 concentrations. Slopes of the weight-loss curves for long exposures were computed by the difference between the 1 and 3 year weight-loss values. The slopes are shown in Table 6 expressed as the equivalent weight loss in a 12 month exposure period and as corrosion penetration in $\mu\text{m}/\text{y}$. Also listed in Table 6 are the hydrogen ion load accumulated during the last 2 years of the sample exposures and the average SO_2 concentration over this period. The corrosion rates do not correlate well when plotted versus H_L because the Washington, DC, data is a distinct outlier from the data for the other sites. On the other hand, there is a good, if nonlinear, correlation with average SO_2 concentration, Fig. 12. Kucera (10) and Byrne and Miller (11) have both indicated that SO_2 and NO_2 can act synergistically under relatively dry conditions to produce sulfuric acid



Kucera has cited evidence of this for carbon steel and copper. Byrne and Miller, based on chemical analyses of corrosion films and condensate, indicate that it could happen on aluminum. Haynie et al. (14) examined the possibility of such a reaction for galvanized steel and found no evidence for one, but the SO_2 and NO_2 levels chosen may not have been suitable for establishing such an effect. Relative to the other sites, the environment at the Washington, DC, site would seem more likely to meet

the conditions needed for Eq. 6 to occur. The Washington, DC, site has the lowest TOW and NO_2 concentrations are high. Furthermore, the runoff measurements indicate that dry deposition of NO_2 occurs on the corrosion film. Thus, a two-layer corrosion film may be a reasonable concept to use in explaining the long-term corrosion behavior of zinc. The stable inner layer then is sensitive to ambient levels of SO_2 and, to a lesser extent, other acidic species in wet and dry deposition (including H_L). Linking of this mechanism to a reaction such as equation 6 would, furthermore, account for the high corrosion rate observed in long exposures at the Washington, DC, site.

CONCLUSIONS

Zinc exhibits different short-term and long-term corrosion effects related to environmental conditions and the nature of the corrosion film. Zinc corrosion in long exposures (exceeding 1 year) depends on atmospheric SO_2 concentration. A synergistic relationship between SO_2 and NO_2 may exist where conditions favor the oxidation of SO_2 to form H_2SO_4 , i.e., relatively dry conditions and significant dry deposition of NO_2 . Zinc corrosion rates are level or increasing in long-term exposures whereas the corrosion film continues to grow. The film growth in long exposures does not improve the corrosion protection and suggests a possible two-layer structure. A stable inner layer sensitive to SO_2 , and perhaps other acidic environmental species including H_L , may control the long-term

corrosion kinetics of zinc. The outer layer is relatively nonprotective, responsive to weathering processes, and continues to grow. In shorter exposures, before the two-layer structure is developed, the corrosion film properties are affected by environmental conditions and this has a strong effect on short-term corrosion performance.

The zinc corrosion film begins transforming into a basic zinc carbonate as soon a corrosion product is formed. $2\text{ZnCO}_3 \cdot 3\text{Zn(OH)}_2$ was identified in the long-term corrosion product. Approximately 8-10 mol pct S relative to Zn was present in the corrosion product for all exposures. Significant amounts of SO_2 and, to a lesser extent, NO_x are deposited by dry deposition. The loss of zinc in runoff from the corrosion film is directly proportional to H_L . In short exposures at the Washington, DC, site, the principal constituent dissolving from the corrosion film was Zn(OH)_2 . In long exposures the principal constituent was ZnCO_3 . The correlation coefficient for rain volume and H_L ranged from weak to relatively strong. In general, covariance was sufficiently low between many of the air quality and rain chemistry variables of interest that problems in developing linear regression models of corrosion damage, may to a considerable degree, be avoided.

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Table 1. - Average pollutant concentrations in
ppb, June 1983 - May 1985.

Site	SO ₂	NO	NO ₂	O ₃
North Carolina	3.0	7.9	12.7	27.3
Washington, DC	10.2	38.4	33.5	17.5
New Jersey	8.3	5.3	15.5	31.8
New York	2.8	0.2	1.3	31.0

Table 2. - Correlations between air quality and rain chemistry variables, July 1983-June 1985.

Interaction	Correlation Coefficients			
	NC	DC	NJ	NY
V - H _L	.62	.42	.84	.50
V - SO ₄ L	.65	.54	.79	.44
V - NO ₃ L	.68	.63	.80	.65
H _L - SO ₂	.06	-.34	-.41	-.26
H _L - NO _x	-.42	-.58	-.34	-.26
H _L - SO ₄ L	.98	.93	.97	.89
H _L - NO ₃ L	.94	.85	.92	.73
NH ₄ L - SO ₄ L	.88	.82	.88	.84
NH ₄ L - NO ₃ L	.94	.88	.84	.77
SO ₂ - SO ₄ L	-.05	-.41	-.48	-.40
NO _x - NO ₃ L	-.55	-.60	-.30	-.20

Table 3. - Wet and dry deposition on zinc (Zn) and stainless steel (SS) at Washington, D.C. in a 1 and 3 month exposure in 1985.

Element/Metal	1 month			3 month		
	Wet	Dry		Wet	Dry	
		$\frac{\mu\text{mol}}{\text{cm}^2}$	pct of total		$\frac{\mu\text{mol}}{\text{cm}^2}$	pct of total
S - Zn	.37	.34	48	.89	.99	53
- SS	.37	.10	21	.89	.20	18
N ¹ - Zn	.33	.16	32	.69	.45	40
- SS	.33	.13	28	.69	.32	32
Ca - Zn	.059	.334	85	.234	1.045	82
- SS	.059	.401	87	.234	1.214	84
Na - Zn	.024	.033	58	.065	.064	50
SS	.024	.022	48	.065	.057	47

¹ N as NO₃; does not include NH₄.

Table 4. - Zinc runoff data from Washington, DC, June - December 1985; H_L - hydrogen ion load, V_L - rain volume load, R - zinc runoff loss from the corrosion film.

Month	H_L , mg H/dm ²	V_L , L H ₂ O/dm ²	R , mg Zn/dm ²	
			observed	fitted ¹
June	.0940	.478	4.27	4.74
July	.0641	.554	3.43	3.96
August	.0643	.574	4.61	4.00
September	.0365	1.441	5.00	5.84
October	.0549	1.088	6.16	5.34
November	.0527	.908	5.00	4.67
December	.0064	.159	1.98	0.73

$$^1R = (a_1 + a_2[H^+])V_L.$$

Table 5. - Effect of H_L and V_L on zinc runoff losses¹.

Independent Variable	V_L coefficient		H_L coefficient		R^2
	α_1	t-score	α_2	t-score	
DC Runoff (short-term)					
H_L only	-	-	70.9	5.8	.85
V_L only	5.09	7.5	-	-	.90
H_L and V_L	3.18	4.8	34.2	3.6	.97
Boldly-exposed (long-term)					
H_L only	-	-	93.2	31.5	.91
V_L	4.21	25.5	-	0	.86
H_L and V_L	0.10	0.2	91.0	6.6	.91

$$^1R_L = (\alpha_1 + \alpha_2[H^+])V_L.$$

Table 6 - Long-term zinc corrosion damage computed
from 12 and 36 month exposure data.

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Site	H _L , mg/dm ²	Avg. SO ₂ , ppb	Annual wt. loss, mg/dm ²	Equivalent corrosion rate, μm/y
New York	0.861 ¹	2.75 ¹	51.5	.72
North Carolina	0.694 ²	3.00 ²	46.3	.65
New Jersey	1.399 ²	8.13 ²	75.9	1.06
Washington, DC	1.270 ¹	10.17 ¹	135.8	1.90

¹Measured June 1983 - May 1985.

²Measured March 1983 - February 1985.

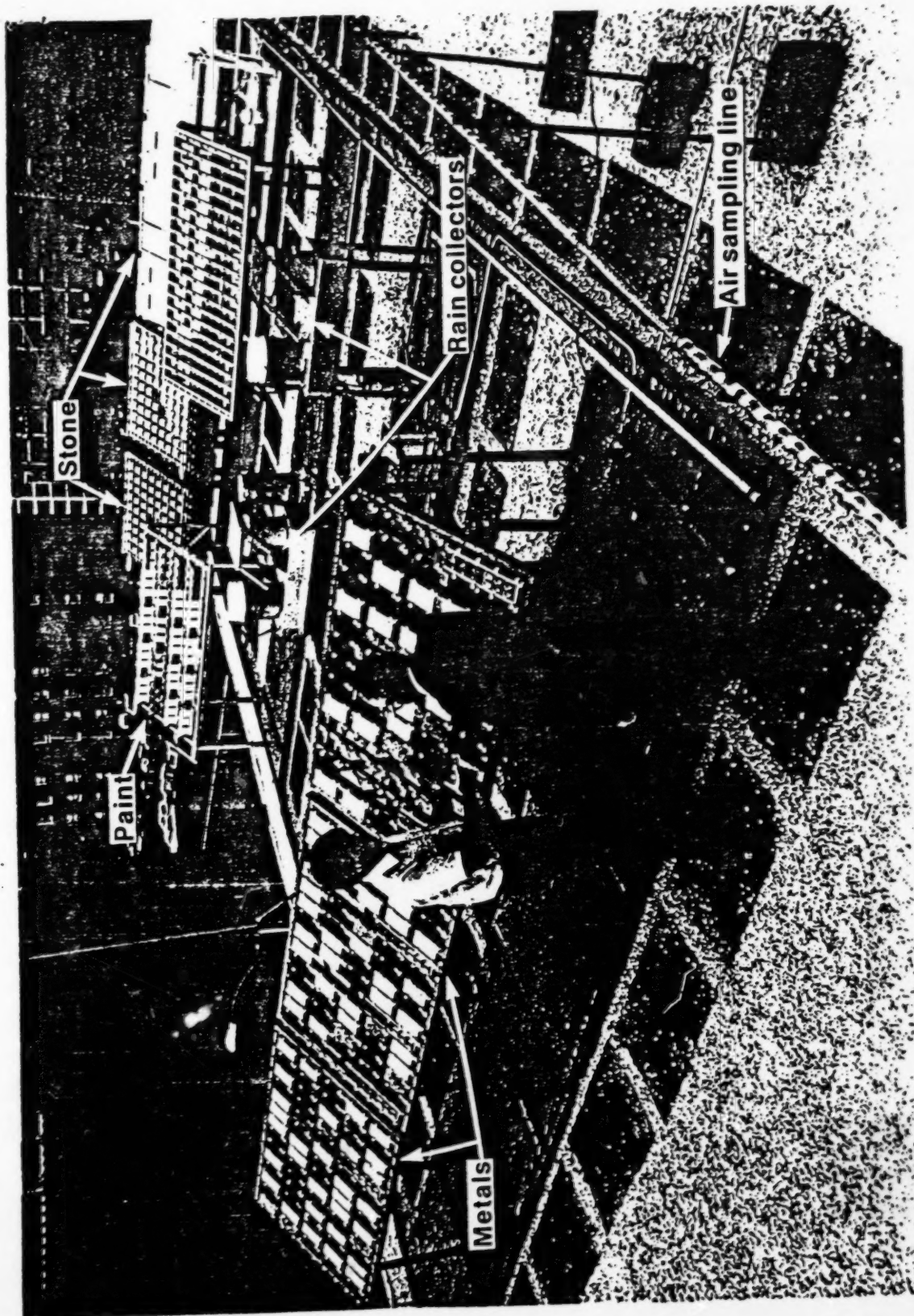


Fig. 1 - Washington, DC, exposure site on roof of West End Library showing: test racks for metal, paint, and building stone; collectors for rain chemistry samples; and sampling line for air quality measurements.

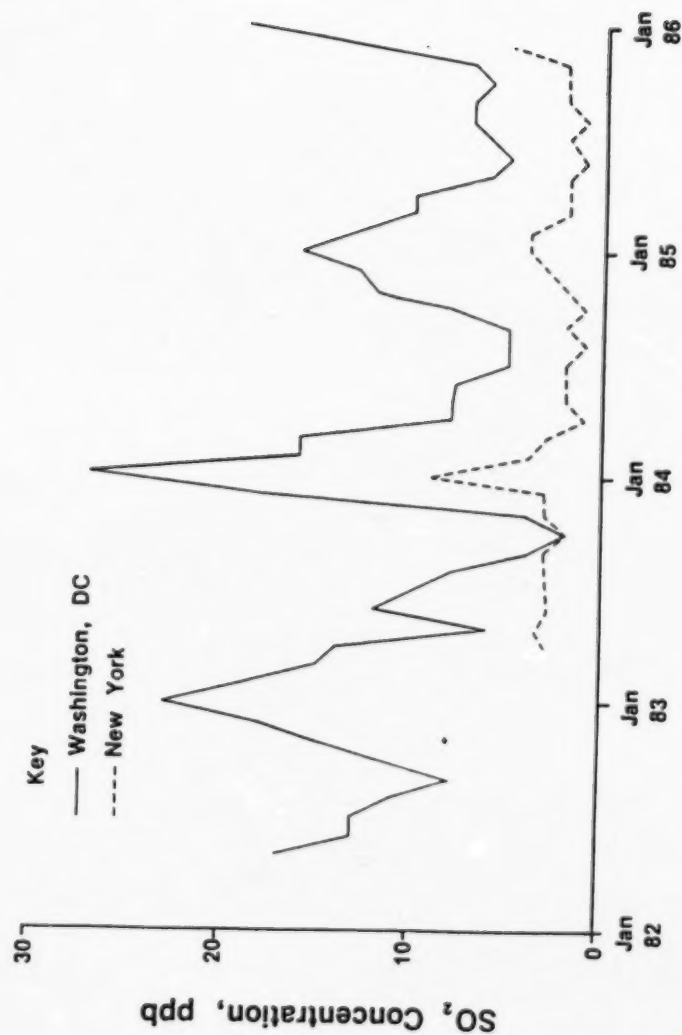


Fig. 2 - Monthly average SO₂ concentrations at Washington, DC, and New York sites; March 1982-December 1985.

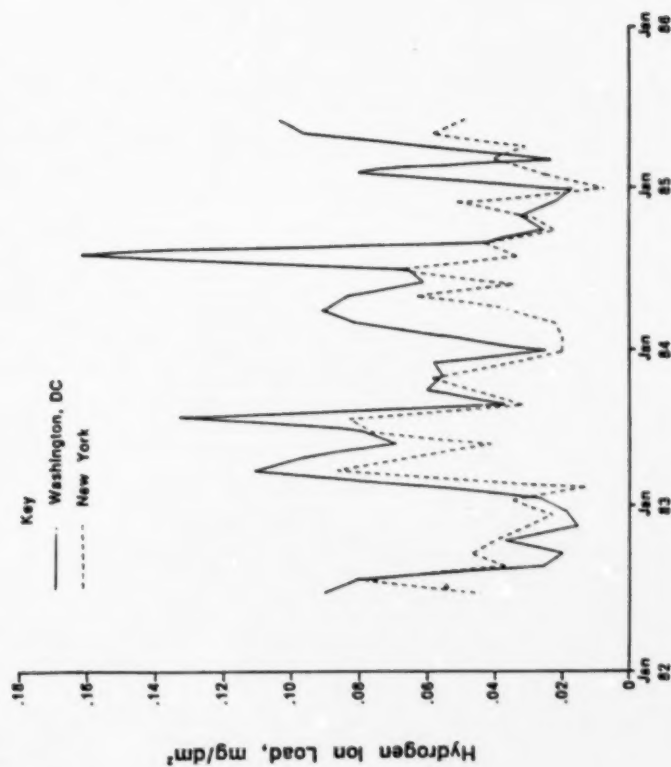


Fig. 3 - Monthly hydrogen ion load at Washington, DC, and New York sites; June 1982-June 1985.

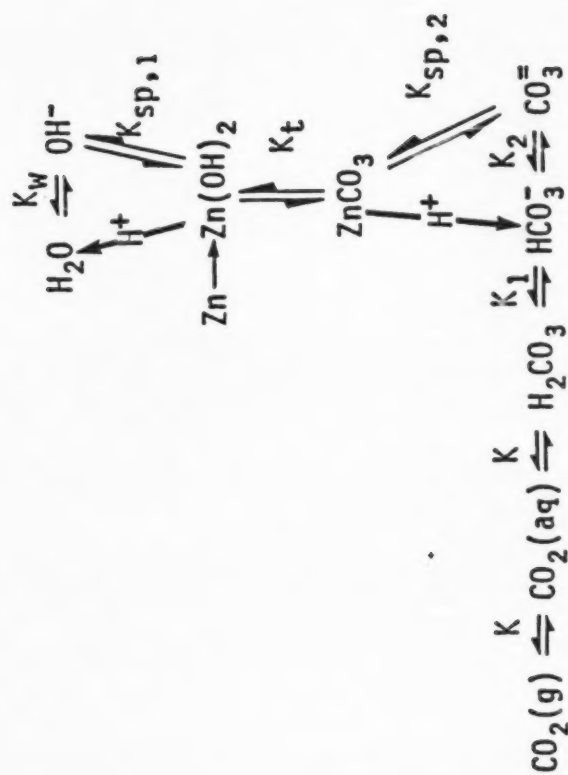


Fig. 4 - Schematic representation of reactions and equilibria involved in forming zinc corrosion film in clean environment.

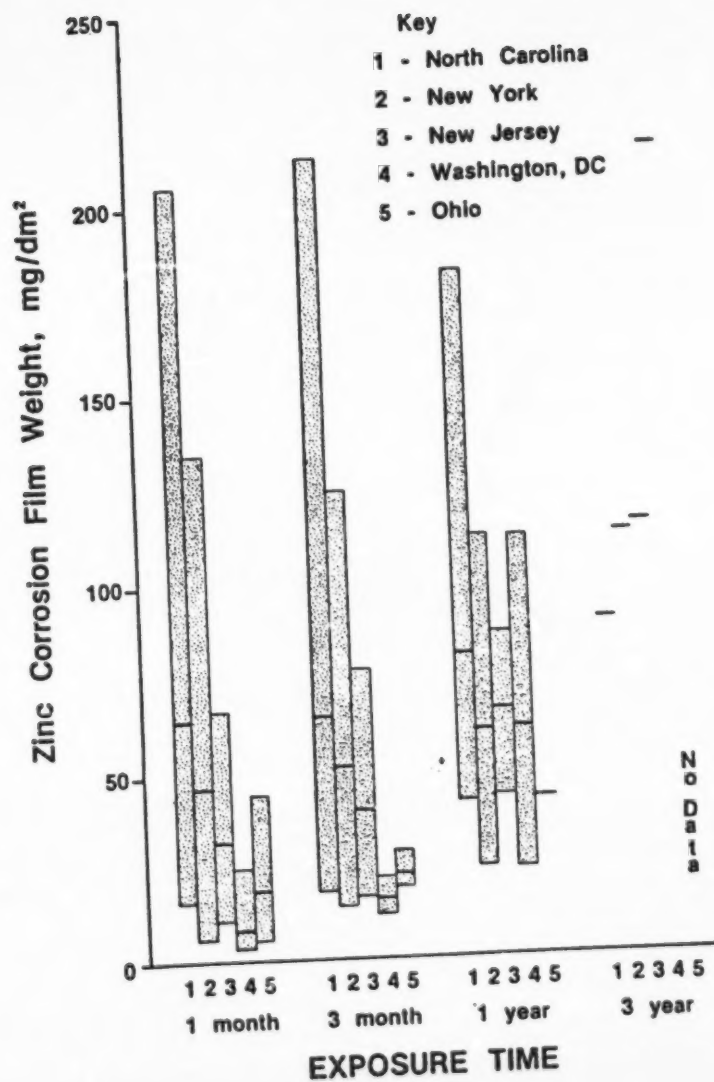


Fig. 5 - Zinc corrosion film weights for 5 field sites and 4 exposure periods. Shaded bar represents the mean film weights for individual tests; horizontal line dividing the bar is average film weight for all tests; March 1982-December 1985.

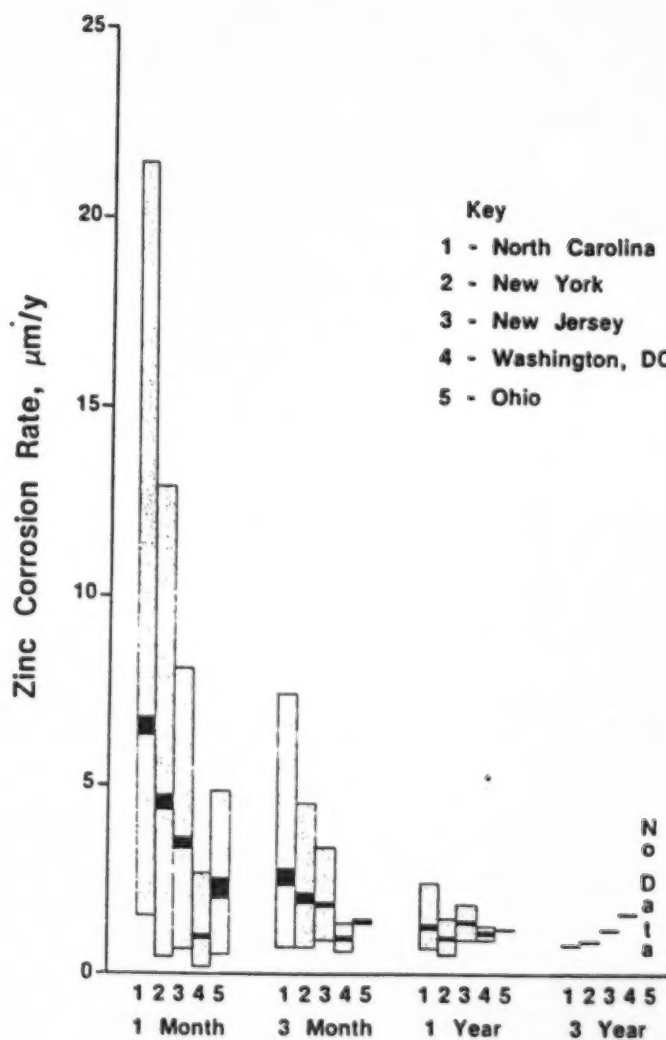


Fig. 6 - Zinc corrosion rates for 5 sites and 4 exposure periods. Shaded bar represents spread in mean corrosion rates for individual tests; solid bar represents standard deviation of replicate measurements; average corrosion rate for all tests is midpoint of solid bar; March 1982-December 1985.

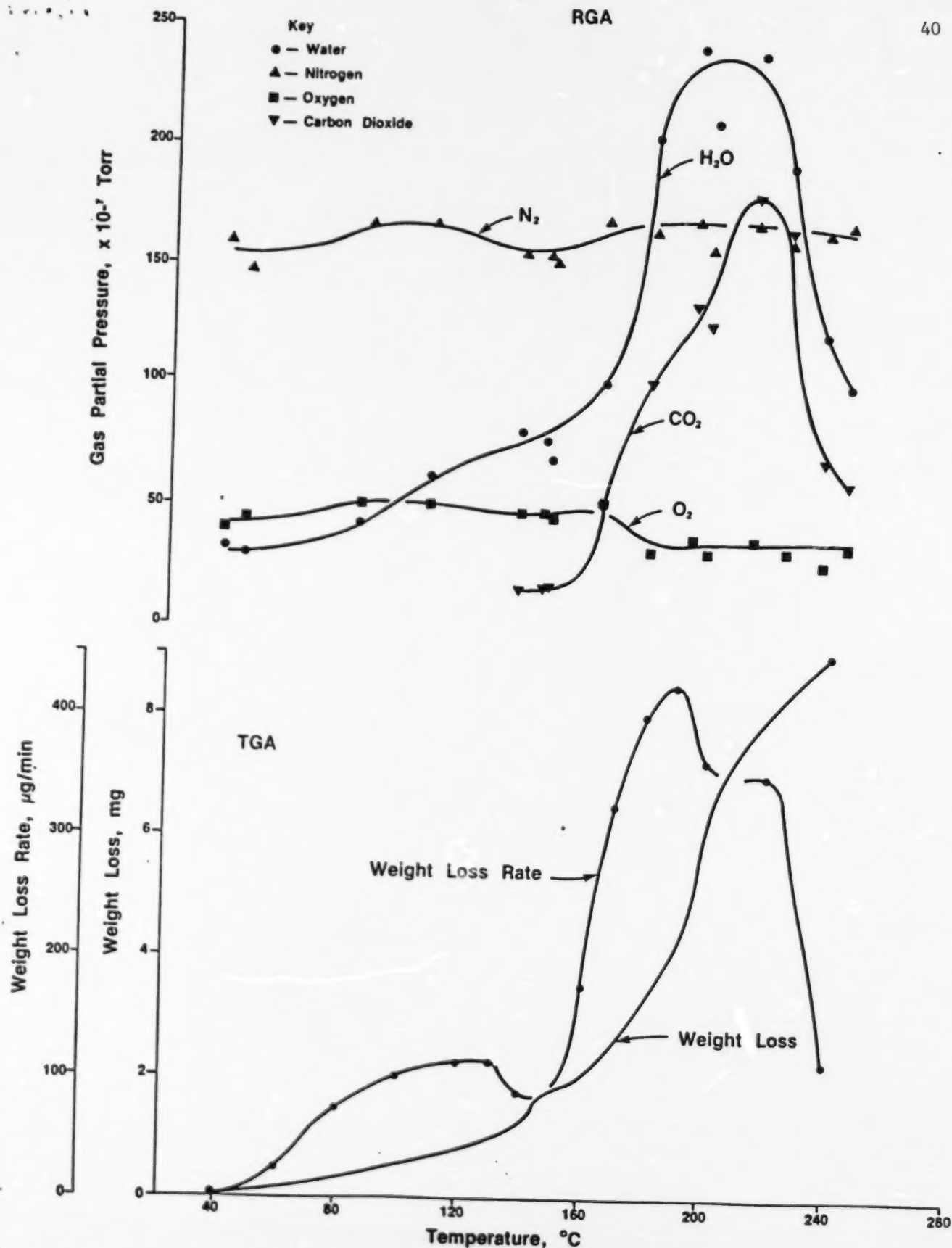


Fig. 7 - TGA and RGA results for corrosion film on zinc microsample C-67 exposed 3 years at the Avondale (MD) methods site.

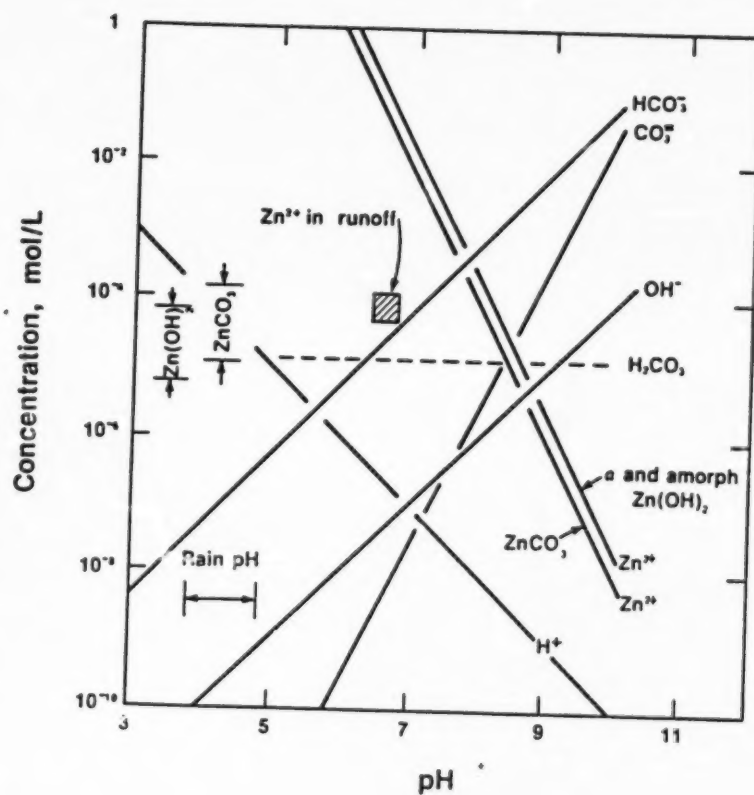


Fig. 8 - Monthly zinc runoff results and related equilibria; June-December 1985.

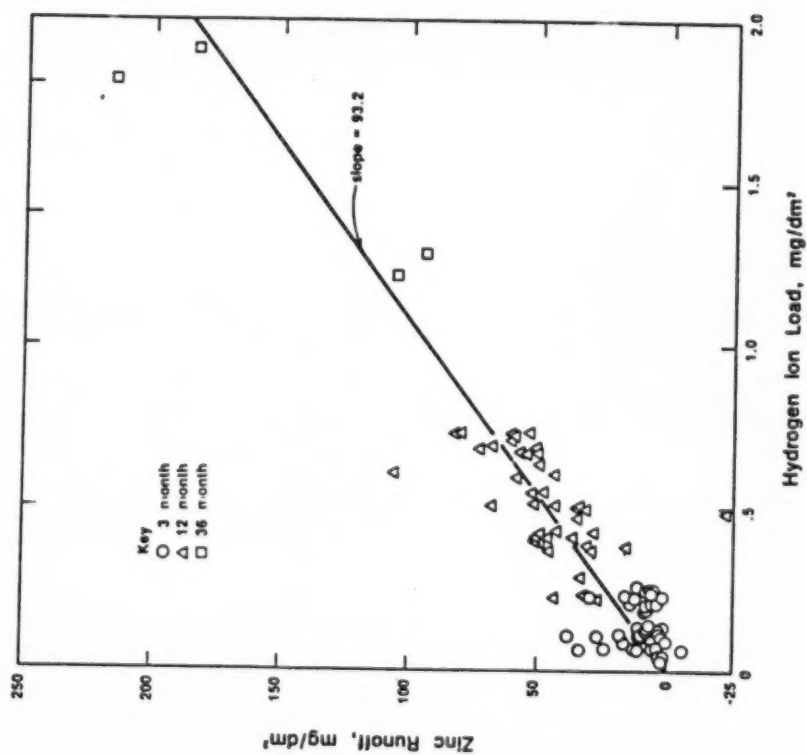
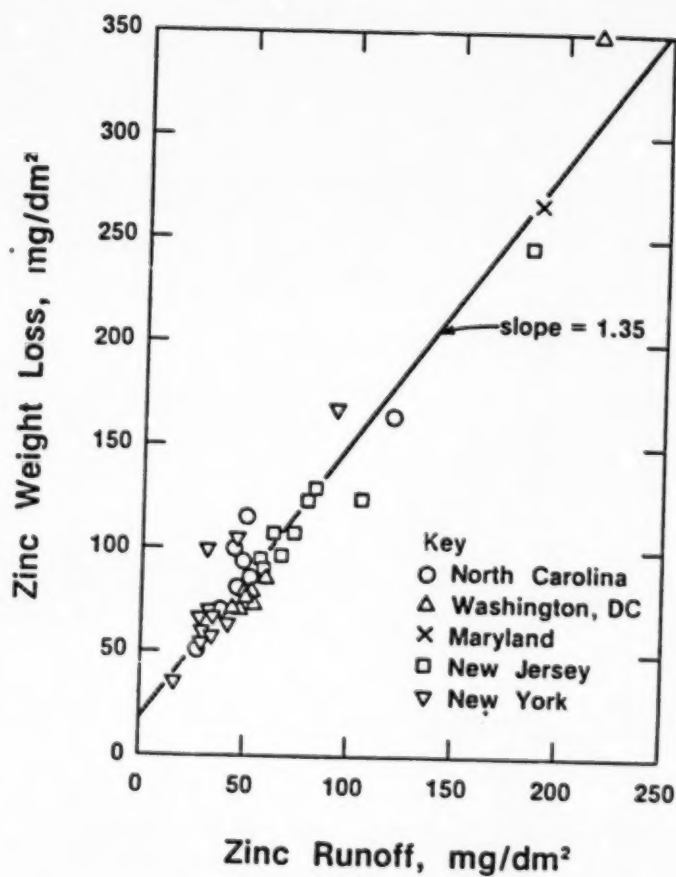


Fig. 9 - Zinc runoff and hydrogen ion loading data from NC, DC, NJ, and NY sites in exposures of 3 months to 3 years; March 1982-December 1985.



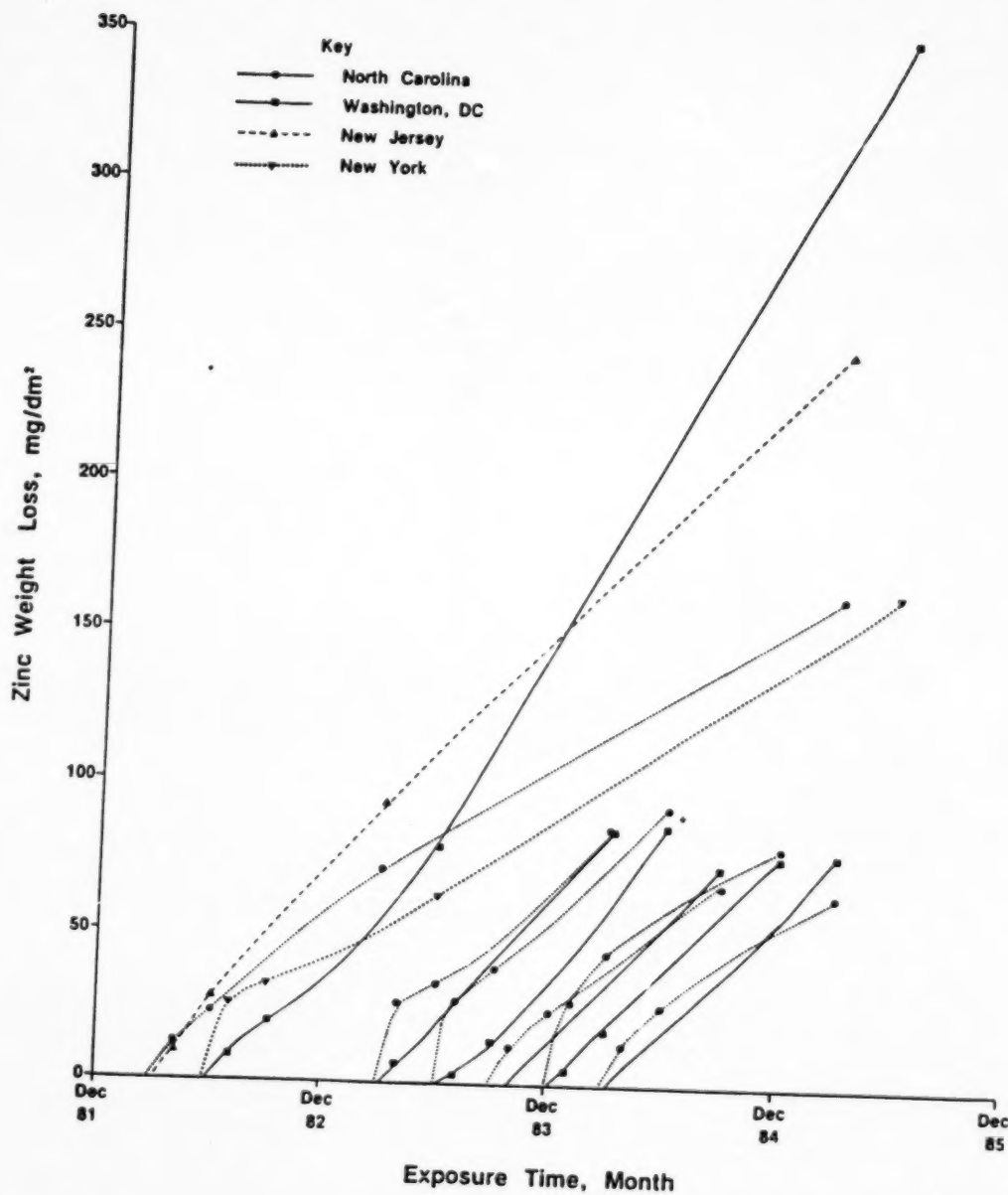


Fig. 11 - Zinc weight loss curves for 3 year exposures at the 4 sites and a series of 1 year exposures at the Washington, DC, and North Carolina sites; March 1982-March 1985.

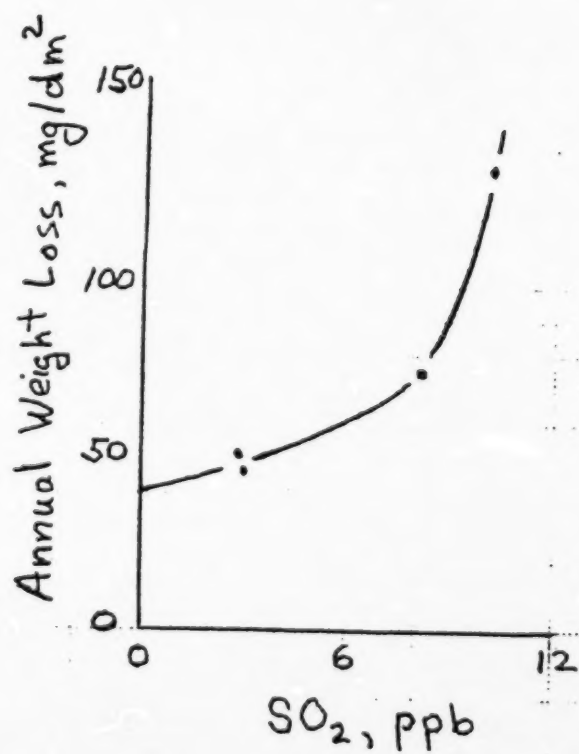


Fig. 12 - Effect of SO_2 concentration on long-term corrosion damage.